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The Chemical Characteristics of Soil Profiles: I. The Podzol.

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The following investigation was carried out in order to determine the qualitative and quantitative chemical differences of the various horizons in podzolized soil profiles by means of methods which envolve the amphoteric nature of the soil complex.

The soils investigated include seven true podzols, three mull podzols (Tamm) or grey forrest soils, and one ground water or meadow soil. Monoliths were taken of the profiles to a depth of 40 cm by means of a specially constructed spade of heavy steel plate shaped into a trough 5 cm deep, 10 cm wide and 40 cm long. The sharpened spade is driven into the ground by a wooden mallet. It is then dug up by means of an ordinary spade and leveled off. A box of galvanized sheet iron of such dimensions that it just fits inside the spade is then placed in an inverted position upon the steel spade, pressed down into the soil which, after turning the spade upside down, is transfered to the box. Fig. 13 shows a series of photopraphs of eight of the monoliths.

Eight of the profiles are from Hallandsås, a ridge on the west coast of southern Sweden with an average annual rainfall of about 700 mm whereas three of the profiles (N:o 5, 6 and 11) are from the vicinity of the Dalälven river in Dalarna in the central parts of the country, with an annual rainfall of about 600 mm. A brief description of the profiles follows:

Description of the profiles.

Profile 1. — Podzolized soil from Tiohaga (I) on the nothern slope of Hallandsås. Beech wood with grass and mosses. About 1 cm litter of beech leaves ect. Drainage good.

A_0. 3.5 cm duff, fibrous.
A_2. 3 to 4 cm grey.
B_1. 12 cm grey-brown.
B_2. 22 cm yellowish brown.
C. Sandy-stony moraine.

Profile 2. — Podzol from Tiohaga (II), in 65 year old spruce plantation about 300 meters north of profile 1. About 2 cm litter of spruce needles. No ground vegetation.

A_0. 8 cm duff, compact.
A_2. 9 cm ash grey.
B_1. 6 cm dark brown.
B_2. 13 cm chocolate brown.
B_3. 24 cm light brown to yellowish brown.
C. Sandy-stony moraine.

Profile 3. — Podzol from Tiohaga (III). Beech wood on a blocky moraine hill about 50 meters west of profile 2. A thick litter of beech leaves between the blocks.

A_0. 9 cm duff, mostly loose F-layer.
A_2. 12 cm ash grey.
A_3. 7 cm darker ash grey.
B_1. 22 cm grey brown.
B_2. 5 cm grey brown sample taken at a depth of 50 cm on top of a large block.

Profile 4. — Podzol from Ljungagården in Tossjö south of Hallandsås in a poor stand of birches some of which were in a dying condition. Ground almost level. Drainage poor. Ground vegetation of vaccinium, grass and mosses. Hardly any litter.

A_0. 3 cm duff, fibrous.
A_2. 7 cm ash grey.
B_1. 24 cm rusty brown to yellowish brown.
B_2. 20 cm yellowish grey.
C. Stony-loamy moraine.

Profile 5. — Podzol from Brovallen in Dalarna. Pine and spruce forest of the vaccinium type with some grasses. Level ground with good drainage. Litter less than 1 cm.

A_0. 2 cm duff, a fibrous F-layer.
A_2. 8 cm light pinkish gray.
B_1. 6 cm dark brown.
B_2. 38 cm rusty brown to yellowish brown.
C. Fine sand.

Profile 6. — Podzol from Djurmo (I) in Dalarna. Spruce forrest of the vaccinium type. Level ground with good drainage. Forest litter about 1 cm.

A_0. 3 cm duff, mostly fibrous F-layer.
A_2. 12 cm light pinkish grey.
B_1. 29 cm rusty brown.
B_2. 14 cm greyish yellow.
C. Medium fine sand.

Profile 7. — Podzol from Axelstorp (I) on Hallandsås, in old beech wood. Profile dug in hollow place into which large quantities of beech leaves are carried by the wind. No ground vegetation. Drainage good.

A_0. 17 cm duff rather sharply divided into an 8 cm loose F-layer and a 9 cm more compact H-layer.
A_2. 8 cm ash grey.
A_3. 14 cm darker grey with lighter spots.
B_1. 40 cm brown.
B_2. 15 cm greyish brown.
C. Sandy-stony moraine.

Profile 8. — Mull podzol from Axelstorp (II) on level elevation about 15 meters from profile 7. The ground vegetation consists of a sparse covering of grass. Hardly any litter.

A_0. 0.5 to 1 cm loose F-layer.
A. 8 cm dark grey.
B_1. 22 cm greyish brown.
B_2. 25 cm yellowish brown.
C. Sandy-stony moraine.

Profile 9. — Mull podzol from Varegården, in beech wood on the northern slope of a divide on Hallandsås. No ground vegetation. A slight amount of litter of leaves and twigs. Drainage good.

A_0. 1 cm loose F-layer.
A_1. 4 cm dark grey.
A_2. 8 cm brownish grey.
B_1. 22 cm brown.
B_2. 20 cm greyish yellow.
C. Sandy-stony moraine.

Profile 10. — Mull podzol from Lyaris on the southern slope and on the opposite side of the same divide in which profile 9 was taken. Profile 10 consists of finer textured material and is drier than profile 9. Beech and hazel with a ground cover of grasses. Litter of dead grass and leaves.

A. 10 cm dark grey mull.
B_1. 28 cm greyish brown.
B_2. 22 cm yellowish brown.
C. Sandy-stony moraine.

Profile 11. — Ground water or meadow soil from Djurmo II, Dalarna. Ground water lewel during the dry season at 40 cm. Vegetation mainly carex.

A_0. 13 cm fibrous duff, compact.
A_2. 27 cm almost white fine sand.
C. Hard bottom moraine.

Samples for the laboratory investigation were collected from each horizon. The depths at which these were taken have been indicated in the figures. The C samples were taken at a depth at which there appeared to be no further change to a lighter color. It is however certain that the B horizon (the horizon of illuviation) extends deeper in most cases. The B horizon investigated is in every case the upper B or B_1.

Methods.

The following determinations were made:

The actual pH (designated pH_0) was determined by the quinhydrone electrode after shaking the soils for half an hour with the minimum amount of water which would yield a fluid suspension.

The ultimate pH (designated pH_u) was determined in exactly the same manner after the soils had been electrodialysed until practically all the extractable anions and cations were removed.

The pH *of exchange neutrality.* This is defined as that pH at which the *electrodialysed* soil complex adsorbs an equivalent quantity of anions and cations from a salt solution and does therefore not affect the pH of the solution. This pH might be termed the »equi-ionic point». This pH differs in different solutions depending on the displacing power of the ions. In previous work (4, VI, X) NaCl and Na_2SO_4 solutions were used but since a divalent cation brings about a complete flocculation at a much lower concentration and since the salt effect should be reduced to the lowest possible value in order to allow the use of the indicator method we have this time employed a n. 0.01 $CaSO_4$ solution.

The buffer capacity for acids and bases and the base combining capacity at pH 7.0, (the latter designated $C_{7.0}$) were found by determining the pH after equilibrium of the soil with solutions of n. 0.01 $CaSO_4$ containing increasing quantities of sulphuric acid on the one side and increasing quantities of

lime water on the other. The procedure was as follows: To each of a series of test tubes 15 cc of a stock solution of n. 0.04 $CaSO_4$ were added. To one of the tubes 45 cc of freshly boiled, distilled water were added whereas a number of the tubes received 45 cc of the water containing increasing quantities of H_2SO_4 and another set of the tubes received 45 cc of lime water of increasing concentration. Five grams of the electrodialysed soil were then added, the tubes stoppered and shaken in the machine for one hour. The pH was determined the following day by the quinhydrone electrode, the latter being immersed into the soil sediment.

A volume of 45 cc allowed the addition of two milliequivalents of $Ca(OH)_2$. Where this was not sufficient to reach a pH of 7.0 as in the case of the humus A_0 horizons, a smaller sample of the soil was taken. Because of the practically complete adsorption of the added base up to and slightly beyond a pH of 7.0 this change in the ratio of soil to solution should not affect the results of the combining capacities which are calculated on the basis of milliequivalents per 100 gram soil.

The adsorption of the base is somewhat greater in the presence of a salt than when added alone to the electrodialysed soil. But since the soil solution always contains a certain amount of salts it appears probable that the base combining capacity when measured in the presence of n. 0.01 $CaSO_4$ (or possibly a somewhat weaker solution) more nearly corresponds to the actual capacity under natural conditions. The results are however on a comparative basis and this is the most important.

Explanation of the figures.

A tabulation of the data would not give a clear picture of the facts because of the great number of determinations envolved. We have therefore decided to present the results graphically as follows:

In figures 1 b to 11 b the abscissa give the number of milliequivalents of H_2SO_4 and $Ca(OH)_2$ contained in 60 cc n. 0.01 $CaSO_4$ whereas the ordinates represent the pH at equilibrium between 5 grams of electrodialysed soil and the 60 cc solutions. The dotted curve represents the pure solution to which no soil was added. The other curves show the buffer capacities of the various soil samples toward acid and base. The points at which the latter curves intersect the solution curve, represent the points of exchange neutrality. Below this point the soil gives rise to an exchange alkalinity whereas an exchange acidity is developed at higher pH values. The point at which a soil curve intersects the line corresponding to a pH of 7.0, gives, when projected on the abscissa, the combining capacity *at this* pH expressed in milliequivalents per 5 grams of soil or, if multiplied by 20, per 100 grams soil (designated by $C_{7.0}$ in figures 1 a to 11 a).

The »curves» in figures 1 a to 11 a show: (1) the pH_0 or the original pH; (2) the pH_u or the ultimate pH; (3) the $C_{7.0}$ values or the base combining capacity at pH 7.0 and (4) the S values or the original *net* base saturation in the different horizons from A_0 to C in the various soil profiles.

The values following the horizon letter, A_0 ect. indicate the depth at which the samples were taken and not the thickness of the horizons, nor do the ordinates represent the depth of the horizons but the latter are instead merely placed equidistant along the ordinate axis. The single values for each horizon are joined by straight lines. The pH_0 and pH_u values are read off at the bottom of the figures whereas the top row of figures give the S and $C_{7.0}$ values. The latter are obtained from the points of intersection of the curves in figures 1 b to 11 b with the pH 7.0 ordinate.

The S values are obtained as follows: The difference between the original and ultimate pH, that is, pH_0 minus pH_u, is calculated. Using the point of exchange neutrality as origin the amount of base necessary to raise the pH to the extent of the calculated difference, where this is positive, is read off

on the corresponding curve in figures 1 b to 11 b. Where the difference is negative, as it is when $pH_0 < pH_u$, the value of S will also be negative, for then acid must be added to lower the pH to the extent of the calculated difference. This is likewise read off on the curves as in the first case. It must however be pointed out that this negative difference becomes measured in terms of a strong acid (H_2SO_4) whereas the greater acidity of the original soil as compared to the electrodialysed, must represent weaker acids and acid salts which, because of their buffer capacity, would require more base per unit pH than is required by H_2SO_4. The negative value of S must therefore in reality be greater than the here calculated value.

Figure 12 shows the average actual pH (pH_0) and the average ultimate pH (pH_u) of the seven true podzols represented in figures 1 to 7 and of an iron and humus podzol from Orsa in Dalarna making an average of eight soils. The average values for pH_0 and pH_u in the various horizons were as follows:

	A_0	A_2	B	C
pH_0	4.00	4.01	4.57	4.87
pH_u	3.25	3.85	4.65	5.18
Difference . . .	0.75	0.16	−0.08	−0.31

As far as the actual pH values are concerned there is a general agreement with results reported by Hesselman (1).

Discussion.

The figures yield a good deal of information, some of which is entirely new but the facts are not easely interpreted for it requires a thorough understanding of the behavior of amphoteric colloids. We shall however attempt to explain the results on the basis of the theory of isoelectric weathering as previously outlined (4, IX). The most startling fact is that

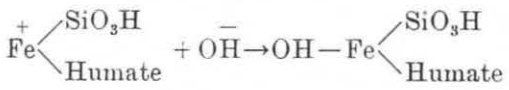
the soil complex in the podzolized profiles is least saturated in the lower horizons and that the actual pH (pH_0) is lower than the ultimate pH (pH_u) in the podzolic C horizons and to a less extent also in the B_1 horizons, leading to a negative *net* base saturation in these parts of the profiles. We shall however leave this, fundamentally so important observation for the present and first turn our attention to the pH of exchange neutrality and the buffer capacity of the soils as represented by the figures 1 b to 11 b.

It will be noted that the pH of exchange neutrality (as also the ultimate pH, comp. fig. 1 a to 11 a) lies in every case higher in C than in the other podzol horizons. The complex is therefore more basic and has a higher isoelectric point in C. Further prove of this was found by cataphoresis. There are three, among other possible factors which account for this fact:

(1) The pH has always been higher in C. This has led to a more extensive ionization and loss through leaching of the acidoid group, chiefly silica, thus leaving a complex with a relatively strong basic residue.

(2) The C horizon contains less of the strongly electronegative humic acids than the B horizon. The humic acids, which move downward from the upper horizons in association with Al and Fe, are always precipitated chiefly in the upper B as often indicated by the chestnut brown color as well as by actual analysis. The ferric and aluminum humates have relatively low isoelectric points (4, IV) and the lower this point the sooner the complex will precipitate when moving as a cation (i.e. positively charged) from a lower to a higher pH, for it is obvious that the lower the isoelectric point of the complex the sooner it will meet with a pH high enough to cause its discharge and precipitation. This applies of course only to the case where the complex exists in a medium whose pH is below that of the isoelectric pH of the complex,

in which case the latter is cationic. We might formulate the process as follows:[1]



cationic complex isoelectric complex.

(3) Ferric complexes are less basic and possess lower isoelectric points than the corresponding aluminum compounds. Ferric complexes precipitate therefore chiefly in the upper B horizon whereas the aluminum complexes move further down, accumulating even in that part of the profile which, because of the absence of a rusty color, is often designated as the C horizon. This accumulation of alumina gives rise to a complex having a strong basic residue and which therefore exhibits a high isoelectric point, a high pH of exchange neutrality and a high ultimate pH.

The pH of exchange neutrality in the B_1 horizons of the true podzols is in every case lower than that of the C horizons. This is as the theory demands, for since the prevailing pH in the B horizon is in general intermediate between that of the C and A horizons, a complex whose composition and amphoteric behavoir is also intermediate, must here accumulate. The position of the pH of exchange neutrality as well as of the other »amphoteric points» will depend upon the ratio of the activity of the acidic residue to that of the basic residue. This ratio will be governed among other things (1) by the ratio of silica and humic acids to sesquioxides and other basic groups, and (2) by the ratio of Al to Fe. A high proportion of alumina means a higher isoelectric point than a high proportion of iron, other things being equal. But the age and the physical condition of the gel affects its amphoteric nature

[1] It is generally assumed that Al and Fe move as complex *anions* associated with hydroxy acids or »protected» by humus. On the basis of this view one could not explain their mobilization at lower and their precipitation at higher pH.

to such an extent that a close correlation to its composition is not to be found.

Of the mineral horizons of the podzols the A horizon has the lowest pH of exchange neutrality and exhibits only weak basic properties. This is due to the fact that, because of the low pH of this horizon, the complex has, through ionization and hydrolytic cleavage, lost a portion of the basic groups.

The organic matter in the A_0 horizon reacts distinctly amphoteric, a fact which we ascribe to the protein and possibly other basic groups of the humus complex.

The point of exchange neutrality constitutes an intensity factor and expresses the qualitative differences between the various horizons. We shall now briefly consider the quantitative aspects of figures 1 b to 11 b as expressed by the capacity to bind acid and base. It will be noted that the B_1 curves mostly intersect the C curves on the acid side and that they always intersect the A_2 curves on the alkaline side of the point of exchange neutrality. This is an expression of the quantity of colloid present in the soil. Per gram colloid the C complex would bind more acid and less base than the B_1 complex, and the A_2 complex would bind less acid and more base than the B_1 complex. On this basis their curves would never intersect. But the B horizon is the horizon of accumulation (illuviation) and contains therefore a higher percentage of colloid. In the case of a profile which has been developed in a uniform parent material it is for this reason obviously impossible for the B_1 and C curves to intersect on the alkaline side and for the B_1 and A_2 curves to intersect on the acid side of the point of exchange-neutrality.

In the cases where the B_1 and C curves do not intersect (on the acid side) it is due either to the accumulation in B_1 being too slight, as in Tiohaga I or Axelstorp II, or it is due to a very much weaker basic residue and a correspondingly stronger acidic residue in B_1, as is evidently the case in Tiohaga II which by its color indicates a humate accumulation in the B_1 horizon.

The slope of the A_0 curves will in the first place be governed by the amount of sand in the humus layer and then also by the nature of the organic matter. The latter is an interesting problem, the solution of which is extremely important.

We cannot here discuss the individual differences as revealed by the different curves because we lack sufficient analytical data, our purpose at this time being merely to study the general characteristics of the podzol type of soil as expressed by the methods we have applied. It is however of interest to note the differences between the true podzols as represented by figures 1 b to 7 b, the mull podzols (grey forest soils) as represented by figures 8 b to 10 b and the ground water soil (fig. 11 b). The nearly identical pH of exchange neutrality in the B_1 and C horizons of the Varegården and Lyaris profiles shows that the extensive chemical differentiation characteristic of the true podzols is here absent. These soils occupy a position between the podzols and the brown forest soils. The greater buffer capacity toward both acids and bases of the B_1 as compared to the C horizons is evidence of a chiefly mechanical accumulation in B. The absence of a humous A_0 layer and instead the distribution of mull throughout the A horizon is also reflected in the curves representing the mull podzols. The curves in fig. 11 b express the chemical relationships within the profile of a ground water soil consisting of a thick humous layer and an apparently homogenous very light colored mineral layer of silt and sand extending down to the very compact bottom moraine. The soil has neither morphologically nor chemically a B horizon and is the product of a high water table. This expresses itself also in the relatively high pH_0 values (comp. fig. 11 a) and the correspondingly high degree of saturation.

We shall now turn our attention to the curves in figures 1 a to 11 a. It will be noted that the combining capacities in the true podzol profiles show in every case two maxima: one in A_0 and one in B_1. The relative magnitude of this capacity in B_1 is a measure of the degree of accumulation in

this horizon, for without, or with only a slight accumulation the base binding capacity would be smaller in the B_1 than in the A horizons because the soil complex in A is always more acidic, has a lower isoelectric point and binds therefore, per gram colloid, the greatest quantity of bases. In the mull podzols the maximum in B may be entirely absent in spite of an accumulation in this horizon because of the distribution of humus throughout the A horizons. In the ground water soil (fig. 11) in which there is no evidence of a layer of accumulation there is also no maximum in the base binding capacity within the mineral horizon.

The pH_0 curves show that the actual pH in the true podzols is always considerably higher in B_1 than in the A horizons. The differences in pH_0 between A_0 and A_2 and between B_1 and C are less definite although the general tendency is an increase in pH as we go downward.

Regarding the ultimate pH (pH_n) we note a steady increase from the A_0 to the C horizon just as in the case of the pH of exchange neutrality.

We have now come to the most interesting question, namely the fact that the actual pH appears in general to be lower than the ultimate pH in the C and B horizons of the podzol profile (see average values fig. 12). This means that the soil contains diffusible acids, removeable by electrodialysis, which are stronger than the acidic residue in the unsaturated (with acids and bases uncombined) colloidal amphoteric complex. The basic residue of the complex must therefore be more or less engaged and to a certain extent saturated with anions. This does not mean that the soil is entirely unsaturated with cations for the two types of combinations overlap more or less, especially in the presence of salts, but the *net* base saturation is < 0 and must therefore be expressed as a negative quantity inasmuch as more base is required to neutralize the original than the electrodialysed soil.

It is generally assumed that the soil in the lower podzol horizons is more saturated with bases than the soil in the

upper horizons. This has been a quite natural conclusion when based on the difference in pH. But we see now that the facts are what appears to be a paradox: The most acidic upper horizons are also the most saturated with bases (comp. the curves designated by S). This could not have been understood before the amphoteric nature of the soil complex was recognized and the relationship between the composition on the one side and the ultimate pH, the isoelectric point and the combining capacity on the other had been worked out (4, IX, X). The theory of isoelectric weathering as previously developed (4, IX) not only accounts for the facts here presented but also leads us to the conclusion that it could not be otherwise.

We shall now apply this theory and attempt to show why the complex which is precipitated in, and builds up the B horizon must be unsaturated with bases and yet give rise to a higher pH as compared to the A horizons of the podzol profile, and further, that the actual pH in the lower horizons must tend to fall below the ultimate pH of the soil complex in these horizons.

The amphoteric cation complex which, in the process of leaching under a cower of sour humus, is mobilized in the upper mineral (A) horizon must be unsaturated with bases because it is formed in a medium whose pH is below that of the isoelectric point of the ion. As it moves downward this ion is bound to lose its charge and precipitate at a pH corresponding to its isoelectric point. The ion can never reach a zone of a higher pH and a correspondingly higher base saturation for in order to do so it would have to pass through a medium whose pH corresponds to its isoelectric pH, and this it could only do if it were a soluble ampholyte. As a matter of fact the cation complex will probably commence to precipitate at a point slightly on the acid side of its isoelectric point when its degree of charge has been reduced to a certain low value. It is therefore clear that any appreciable base saturation will never be met with in the B horizon of a

podzol profile. The pH in this horizon will nevertheless be relatively high because the horizon has been built up by the basoid material from the A horizon which, because of the low pH which there prevails, becomes ionized and split off by a hydrolytic cleavage to follow the movement of the ground water.

The pH in the C horizon may have any value depending upon the parent material but even in the absence of carbonates the pH is here likely to be the highest in the profile. The complex which is here formed in the process of hydrolysis will therefore posses a relatively high proportion of sesquioxides because a large proportion of the silica will be mobilized and lost together with the strong bases. The complex will therefore possess a relatively strong basic residue, a high isoelectric point and a high ultimate pH. But the complex in C will be quantitatively much smaller than in B and will therefore posses a lower buffer capacity towards acids as well as towards bases even though the buffering effect of the complex toward acids be qualitatively the greatest. In the absence of carbonates and in sandy parent material, which is the type here investigated, the buffer capacity of the C horizon is therefore so low that the soil complex will soon fall offer for a complete unsaturation with bases.

If we now consider that the soil solution which leaches down from the upper horizon of sour humus is more or less charged with acids, both mineral and organic, it is readily understood why the actual pH of the soil solution in the B and C horizons is lower than the ultimate pH of their colloidal complexes and why the latter become negatively saturated with bases. We can also understand why the actual pH as compared to the ultimate pH is lower in the C than in the B horizon because the greater buffer capacity of the B horizon has a greater effect upon the pH of the solution. An amphoteric colloid always causes a change of the pH of a solution in the direction of the isoelectric point and does so in proportions to the concentration of the colloid. If we

were to shake soil samples from the B and C horizons with a solution having a pH equal to that of the A horizons we should get exactly the same results. The new pH would lie between the original pH of the soil and of the solution, and would be nearer that of the soil the greater its colloidal content.

The facts as observed lead to another, in the nature of the process of podzolization, necessary consequence. Podzolization is a dynamic process which, as long as its causes are operative proceeds ever further. The A_2 horizon advances downward pushing the B horizon deeper which in turn encroaches upon the C horizon. If now the pH of the B and C horizons did not fall below the isoelectric point and ultimate pH of their respective complexes there could be no translocation of material and no downward displacement of the horizons. The speed of this displacement will, other things being equal, depend upon the buffer capacity of the parent material. It will be rapid in sand, slow in clay and in the presence of carbonates.

Figure 12 which represents the average pH values in eight true podzol profiles indicates that a pH of 4.0 in the humus layer is fatal to the mineral complex in the lower horizons in that it brings about its desaturation with strong bases and then an acid hydrolysis of the complex by ionizing and mobilizing its basic groups, resulting in the characteristic, bleached A_2 horizon. The podzolization has a quantitative as well as a qualitative aspect however, for although the pH in the humus layer be low the process will not be marked unless a sufficient quantity of humus is formed. Thus in the Axelstorp II profile (fig. 8) the pH in the one cm thick humus layer was 4.02 but the profile is only slightly podzolized whereas three of the true podzols had a higher pH in the humus layer.

The Axelstorp I profile (fig. 7), dug in a hollow place, about 15 meters from the Axelstorp II profile, where large quantities of beech leaves accumulate yearly, has a humus layer of 18 cm (pH 3.65) and is strongly podzolized. The same is

true of the Tiohaga III profile (fig. 3) which was dug between large blocks in a beech wood on moraine. Many leaves had accumulated between the blocks and the leaching was here undoubtedly greater than corresponds to the rainfall because of the many blocks scattered on and below the surface. Both of the profiles were very deep although the accumulation in the B horizons was not so marked. The Tiohaga II (fig. 2), dug in a 65 year old spruce plantation about 50 meters from Tiohaga III, was more shallow although fully as mature as the two beech wood podzols. If we compare the actual and ultimate pH of the humus in these profiles, one is led to the conclusion that it makes little difference what the nature of the original organic matter (the litter) is, as long as the conditions are such as to favor the formation of humic acids in large excess of the bases available for neutralization. We shall not further discuss the individual differences between the various profiles at this time because this requires a more detailed investigation of a greater number of profiles which we hope to be able to present later.

There are however certain other considerations which apply to the podzol profile in general, which deserve our attention. In the first place the fact that the most acidic A_0 horizon is always positively saturated with bases and contains often considerable quantities of these, is of special interest. That the humic complex can posses a relatively high degree of saturation in spite of the low pH depends upon its strongly acidic nature and, compared to other colloids, its low equivalent weight (1 gram of humic acid neutralizes about 3 milliequivalents of base). But the humus horizon contains more bases than correspond to the degree of saturation of the *colloidal* organic complex. Electrodialysis of samples from the podzol A_0 horizons yields always considerable quantites of bases on the one side and soluble organic acids together with some mineral acids on the other. Some of the bases exist therefore in combination with organic acids of the more simple and soluble type.

But while considerable quantities of bases may be stored up in the humus, as compared to the very much smaller quantites of the other podzol horizons[1], these bases or metal cations are of little direct benefit because their release envolves a still further lowering of the pH. If however the conditions which favor the production of humic and other organic acids should be succeded by conditions which favor the complete decomposition of the organic matter into water and carbon dioxide we can easely foresee some of the immediate results. After the destruction of some of the humic acids the residue would attain a higher degree of base saturation and the pH would increase. A moderate decomposition would raise the pH to that of the isoelectric points of the mineral complexes in the lower horizons. The acid hydrolysis would then cease, less bases would be lost by leaching and the soil complex would become positively saturated with bases throughout the profile. The sesquioxides would no longer be mobilized in the A horizon but would on the contrary be precipitated in combination with the very acid complex in this horizon and would therefore tend to accumulate, resulting in a regeneration of the podzolized horizon (4, XV).

The natural causes leading to a regeneration of the podzol profile have been observed and described by Lundblad (2) and by Tamm (5). We have here merely wished to give a brief outline of the chemistry of this regeneration as based on earlier experiments and on the theory of isoelectric weathering.

The results of our investigation have shown that it is possible to characterize a soil by an expression of the chemical nature of the amphoteric soil complex in the various parts of the profile. This method possesses obviously a great advantage over the various methods which envolve a chemical analysis of the soil or the solution of the colloids by various reagents. The analysis of the whole soil yields in general very little information and besides, is too slow and expensive. The

[1] Electrodialysis removed from 12 to 24 times more bases from the A_1 than from the B or C horizons of the true podzols.

trouble with the chemical extraction of the »colloid» is that the colloid is not extracted but suffers a partial decomposition, the products of which by no means correspond to the proportion of the constituents in the original colloids. This is true whether we use ordinary dilute acids or alkali, the acid oxalate method of Tamm or the 5 % K_2CO_3 extraction used by Gedroiz.

The extracted ratio of silica to sesquioxides depends primarily upon the pH of the solution and upon the nature of the colloid, that is, its composition and isoelectric point. The more acid the solution and the higher the isoelectric point of the colloid, other things being equal, the lower the ratio of silica to sesquioxides in the extract. The acid oxalate used by Tamm has a pH of 3.25 and yields accordingly a low ratio in the extract. Lundblad (3), working in the senior authors laboratory in New Brunswick found the following ratios in the acid oxalate extract from three American soil colloids (separated from the soil by the supercentrifuge):

Colloid:	Sharkey	Sassafras	Nipe
$\frac{SiO_2}{R_2O_3}$ in the original colloid . .	3.18	1.89	0.31
$\frac{SiO_2}{R_2O_3}$ in the oxalate extract . .	0.54	0.16	0.10
Percent colloid dissolved	4.07	7.86	6.34

Using a mixture of HCl in n. 0.2 NaCl the senior author extracted the following ratios from the Sharkey soil at different acidities:

pH of extract: .	3.03	3.51	4.14	4.56	6.55
$\frac{SiO_2}{R_2O_3}$ ratio: . . .	0.72	1.00	2.17	4.97	∞

The work of Lundblad shows that the extracted material corresponds neither qualitatively nor quantitatively to the colloid and the experiments by Mattson, which will be published

later in greater detail, show how greatly the results are affected by the pH. The latter experiment is of special interest in that it illustrates the natural process of weathering: The lower the pH the greater is the ionization and mobilization of the basic groups of the complex, resulting in a residue richer in silica. Conversely, the higher the pH the greater the ionization and mobilization of the acidic groups, resulting in a residue richer in sesquioxides. The former process is represented by podzolization and the latter by laterization. Both are explained by the theory of isoelectric weathering. According to this theory the soil complex will tend to alter its composition in such a way that its isoelectric point coincides with the pH of the soil solution.

Summary.

A series of seven true podzols (fig. 1—7), three mull podzols (fig. 8—10) and one ground water soil (fig. 11) have been studied with respect to the following characteristics of the various horizons of the soil profiles:

(1) The actual pH (pH_0) of the soil.
(2) The ultimate pH (pH_u) or the pH of the soil after complete electrodialysis.
(3) The pH of exchange neutrality or the equi-ionic point, defined as that pH at which the unsaturated (electrodialysed) soil combines with an equal number of the anions and cations of a neutral salt and does therefore not affect the pH of the solution.
(4) The buffer capacity toward acids and bases and the base combining capacity at pH 7.0 (designated $C_{7.0}$).
(5) The degree of saturation (S) of the soil.

The most outstanding facts are:

(1) The pH of exchange neutrality as well as the pH_u is highest in the C, lower in the B and lowest in the A horizons.
(2) The base combining capacity of the true podzols has two maxima, the one in A_0 and the other in B.

(3) In the lower horizons (B and C) of the true podzols the actual pH is lower than the ultimate pH (fig. 12).

(4) The lower horizons possess a zero or negative base saturation, this in spite of the fact that their pH is considerably higher than that of the upper horizons. The sour humus layer A_0 possesses an appreciable base saturation.

These facts can all be satisfactorily explained on the basis of the theory of isoelectric weathering.

Den podsolerade markprofilens kemiska karaktär.

Resumé.

Sju podsolprofiler, tre mullpodsolprofiler och en sumpjordmånsprofil, samtliga på sand eller sandig morän från Dalarna resp. Hallandsåsen hava undersökts med hänsyn till följande egenskaper:

(1) De olika horisonternas ursprungliga pH-värde, i figurerna betecknat med pH_0.

(2) Jordprovens pH-värde efter fullständig elektrodialys, det s. k. gräns-pH-värdet (ultimate pH), i figurerna betecknat med pH_u.

(3) Den elektrodialyserade, med anjoner och katjoner omättade jordens utbytesneutralitetspunkt, eller det pH-värde, vid vilket markgelen adsorberar ett lika stort antal av ett neutralsalts anjoner och katjoner och därför ej åstadkommer någon förskjutning av lösningens pH. Denna punkt sammanfaller med det pH, vid vilket $CaSO_4$-kurvan i fig. 1 b—11 b skäres av ($CaSO_4$ + jordprovs)-kurvan.

(4) Den elektrodialyserade jordens bufferkapacitet mot syra och bas samt den vid neutralpunkten bundna basmängden (jordens katjonutbyteskapacitet vid pH 7.0). Det senare värdet för de olika horisonterna angives i fig. 1 b—11 b i milliekvivalenter $Ca(OH)_2$ per 5 gram jord. I fig.

1 a—11 a är värdet angivet i milliekvivalenter $Ca(OH)_2$ per 100 gram jord och är där betecknat med $C_{7.0}$.

(5) Jordens ursprungliga basmättningsgrad, i fig. 1 a—11 a betecknad med S. Denna är beräknad genom att i fig. 1 b—11 b avläsa den mängd bas eller syra, som erfordras för att höja eller sänka den elektrodialyserade (omättade) jordens pH-värde (pH_u) till dess ursprungliga pH-värde (pH_0). Där pH_0 är lägre än pH_u blir basmättningsgraden negativ. Detta är fallet i podsolprofilens B- och C-horisonter.

Av undersökningen framgår följande, med teorien om den isoelektriska vittringen överensstämmande lagbundenheter:

(1) Utbytesneutralitetspunkten i podsolprofilen ligger högst i C-, lägre i B- samt lägst i A-horisonten. Detta beror därpå, att det rådande pH-värdet är högst i de djupare horisonterna, vilket leder till att markkolloidernas sura grupper företrädesvis joniseras och utlakas, i första hand kiselsyra. Kolloidkomplexen bli härigenom rikare på basiska grupper, huvudsakligen aluminium och järn, vilket leder till en hög isoelektrisk punkt, ett högt pH_u samt en hög utbytesneutralitetspunkt. De komplex, som utfällts i anrikningshorisonten B, ha likaledes en hög isoelektrisk punkt, ty de bestå till stor del av basiska grupper, vilka i den surare A-horisonten undergått en katjonisk jonisering samt vandrat nedåt till dess de utfällts vid ett pH, som motsvarar deras isoelektriska punkt.

(2) Förmågan att binda syror är i allmänhet störst i B trots att C-komplexen äro mera basiska. Detta beror på att B-horisonten till följd av anrikningen ovanifrån är rikast på kolloider. Förmågan att binda syror är mycket låg i A-horisonterna, ty deras kolloider äro starkt sura och ha därför en mycket låg isoelektrisk punkt. Förmågan att binda baser är större i B än i A_2 (blekjorden), trots de betydligt surare komplexen i den senare. Även detta beror på den stora kolloidanrikningen i B. Det hela är därför en kvantitativ företeelse, ty kvalitativt, d. v. s. per

gram kolloid räknat, besitta alltid A-komplexen en större basbindande förmåga än både B och C. Denna förmåga är störst i A_0 (humusskiktet).

(3) I podsolprofilerna finner man därför två maxima med hänsyn till katjonutbyteskapaciteten (fig. 1 a—7 a, $C_{7.0}$), medan mullpodsolprofilerna oftast sakna ett B-maximum, delvis till följd av en svagare anrikning i B och delvis emedan mullen är här fördelad i hela A-horisonten (fig. 8 a—10 a, $C_{7.0}$).

(4) Gräns-pH-värdet (pH_u) stiger, samtidigt med utbytesneutralitetspunkten, i riktning mot de djupare horisonterna, vilket sammanhänger med en minskning av kolloidkomplexens sura grupper samt en ökning av deras basiska grupper. Detta åstadkommer även en höjning av den isoelektriska punkten (jämför fig. 12, som angiver medeltalsvärden av åtta podzolprofiler).

(5) Det ursprungliga pH-värdet (pH_0) i humusskiktet är, trots dettas surhetsgrad, betydligt högre än pH_u. Humustäcket har därför, jämfört med mineraljorden, den största basmättningsgraden (S). I A_2 är skillnaden ej stor. I B- och C-horisonterna ligger, med undantag av sumpjordsprofilen, det ursprungliga pH-värdet lägre än den elektrodialyserade jordens pH-värde. Basmättningsgraden får här ett negativt värde till följd av ett överskott av diffunderbara, fria syror.

Att basmättningsgraden är lägst eller rent av negativ, där pH-värdet är högst torde betraktas som en paradox. Men förhållandet är lätt förklarligt om man tar hänsyn till markkolloidernas amfotära karaktär. Den isoelektriska punkten är hög i B och C. Jordens pH-värde kan därför vara jämförelsevis högt utan någon nämnvärd basmättning. Kolloiderna i podsolprofilens B-horisont måste alltid vara omättade med baser, ty dessa kolloider äro i huvudsak bildade genom utfällning av i A-horisonten joniserade och utlakade katjonkomplex. Då nu dessa katjonkomplex äro mättade med syror i stället för baser

och då de urladdas och utfällas så snart de nå ett medium, vars pH-värde ligger nära deras isoelektriska punkt, så är det ju tydligt, att de aldrig uppnå en nämnvärd basmättning. Att pH_0 är lägre än pH_u i podsolens B- och C-horisonter beror tydligen därpå, att den från A nedsilande markvätskan har ett lägre pH-värde än B- och C-kolloidernas pH_u-värde. De med baser omättade kolloiderna i B och C binda delvis de fria syrorna, uppnå en surare reaktion samt visa en negativ basmättning.

References.

(1) Hesselman, H. Studien über die Humusdecke des Nadelwaldes, ihre Eigenschaften und deren Abhängigkeit vom Waldbau. Meddel. Statens Skogsförsöksanstalt (Sweden 22: 167—552. 1926).

(2) Lundblad, K. Ein Beitrag zur Kenntnis der Eigenschaften und der Degeneration der Bodenarten vom Braunerdetypus in südlichen Schweden. Meddel. Statens Skogsförsöksanstalt 21: 1—48. 1924).

(3) Lundblad, K. Studies on Podzols and Brown Forest Soils: I. Soil Sci. 37: 137—155. (1934).

(4) Mattson, Sante. The laws of soil colloidal behavior:

IV. Isoelectric precipitates. Soil Sci. 31: 57—77. (1931).

VI. Amphoteric behavior. Soil Sci. 31: 343—365. (1931).

IX. Amphoteric reactions and isoelectric weathering. Soil Sci. 34: 209—240 (1932).

Mattson, Sante and Hester, Jackson, B.

X. Exchange neutrality and combining capacity. Soil Sci. 34: 459—482 1932).

XV. The degradation and regeneration of the soil complex. Soil Sci. (1934).

(5) Tamm, Olof. Der braune Waldboden in Schweden. Proc. Second Intern. Congress of Soil Science (Leningrad—Moscow 1930). Commission V: 178—189. 1932).

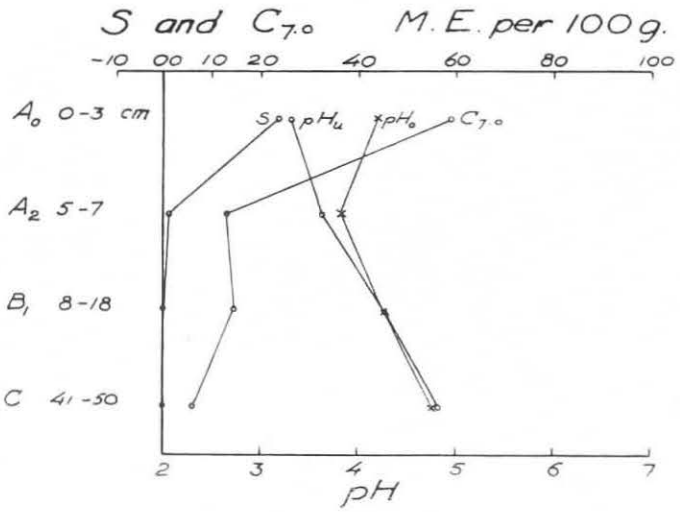


Fig. 1 a. Profile 1. The actual pH (pH_0), the ultimate pH of the electrodialysed soil (pH_u), the base combining capacity at pH 7.0 ($C_{7.0}$), and the base saturation (S) in the different horizons of the soil profile. The figures to the left give the dephts in cm. at which the samples were taken.

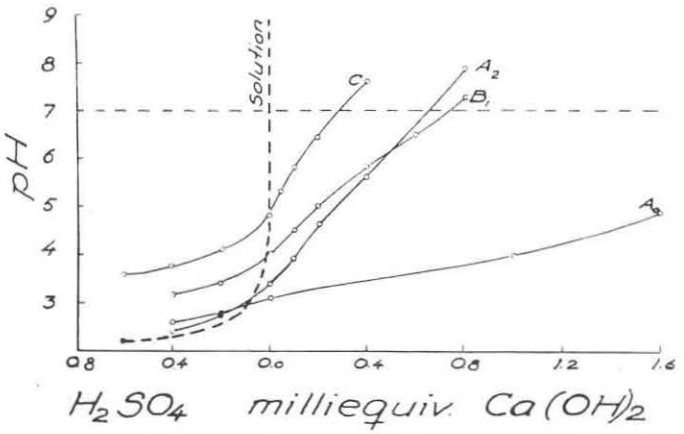


Fig. 1 b. Profile 1. The pH of exchange neutrality (the point at which the soil curve intersects the solution curve) and the buffer capacity of the electrodialysed soil toward H_2SO_4 and $Ca(OH)_2$ in a n. 0.01 $CaSO_4$ solution. Five grams of soil in 60 cc solution.

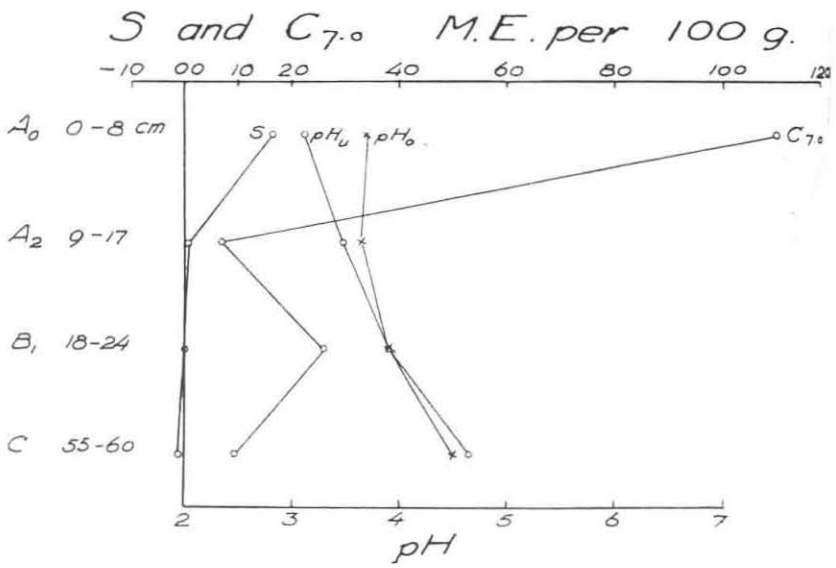


Fig. 2 a. Profile 2. For legend, see fig. 1 a.

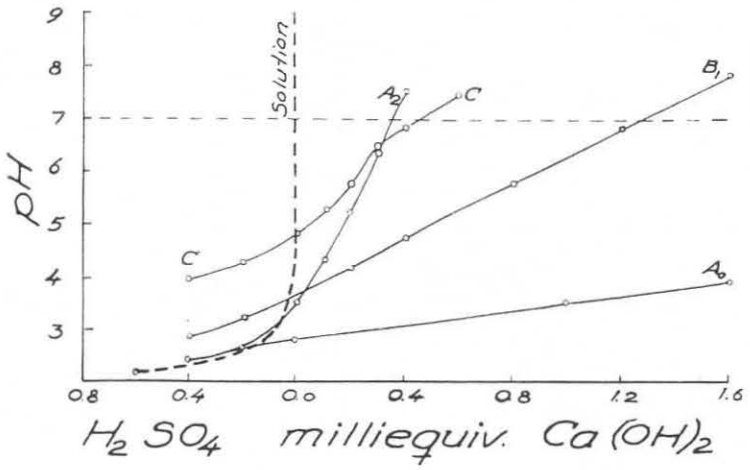


Fig. 2 b. Profile 2. For legend, see fig. 1 b.

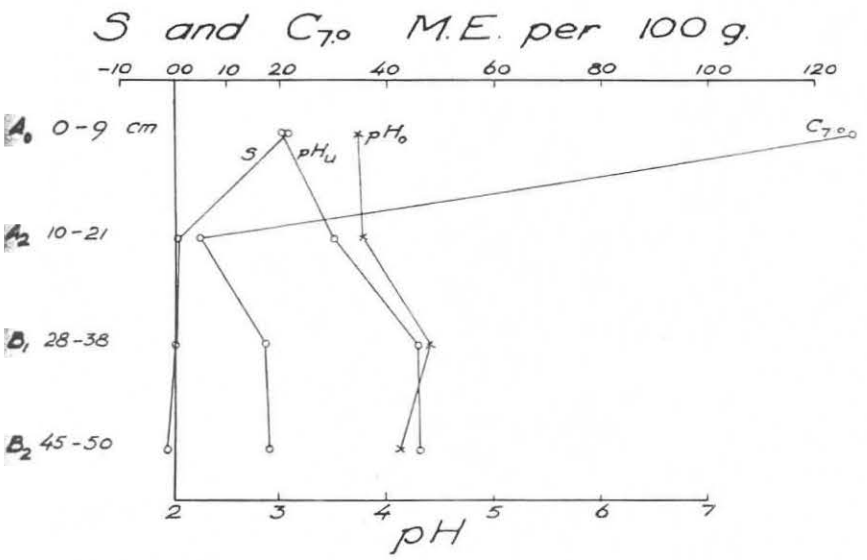


Fig. 3 a. Profile 3. (For legend, see fig. 1 a.

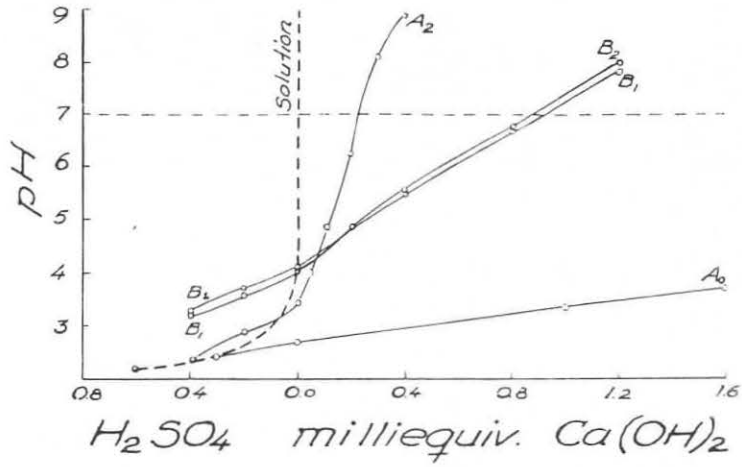


Fig. 3 b. Profile 3. (For legend, see fig. 1 b.

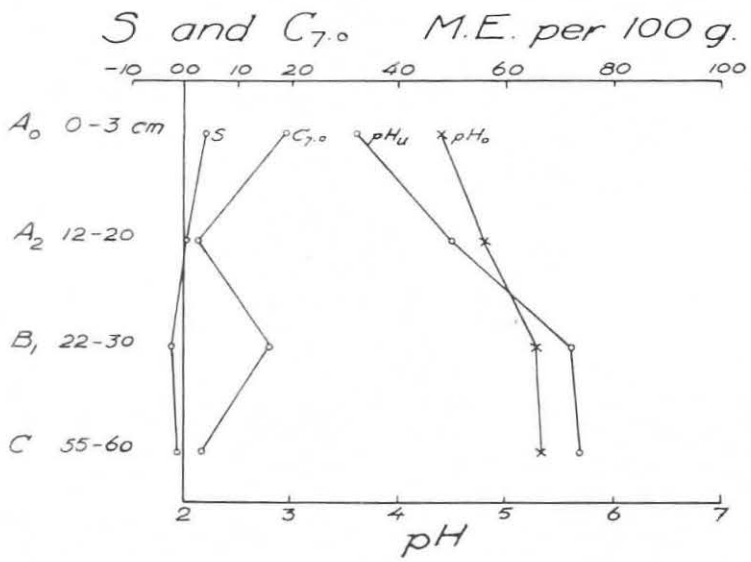


Fig. 4 a. Profile 4. (For legend, see fig. 1 a.)

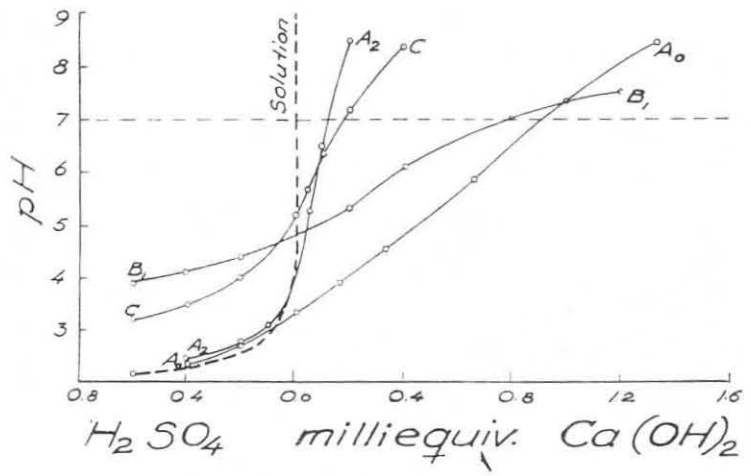


Fig. 4 b. Profile 4. (For legend, see fig. 1 b.)

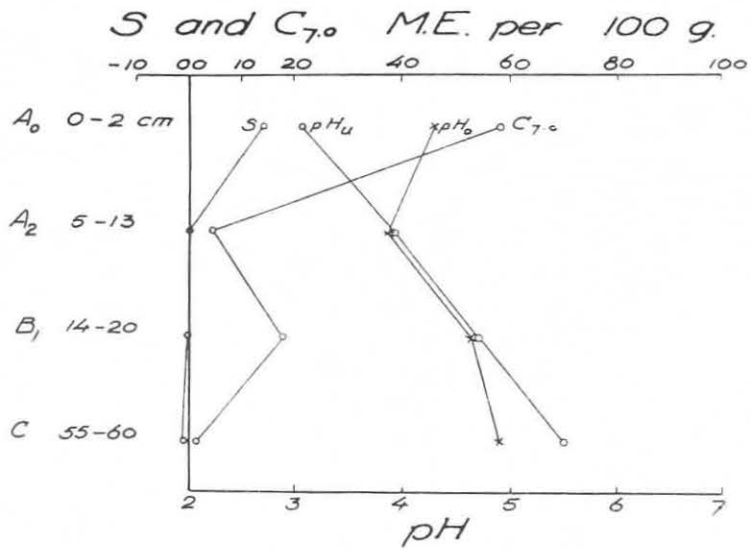


Fig. 5 a. Profile 5. (For legend, see fig. 1 a.

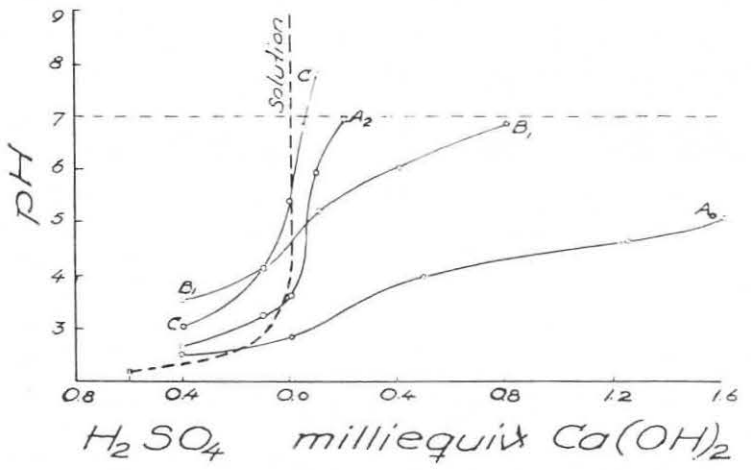


Fig. 5 b. Profile 5. (For legend, see fig. 1 b.)

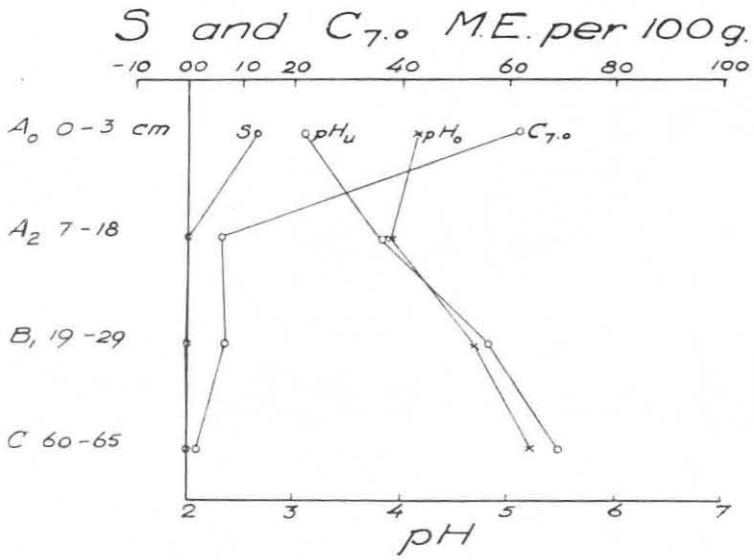


Fig. 6 a. Profile 6. (For legend, see fig. 1 a.)

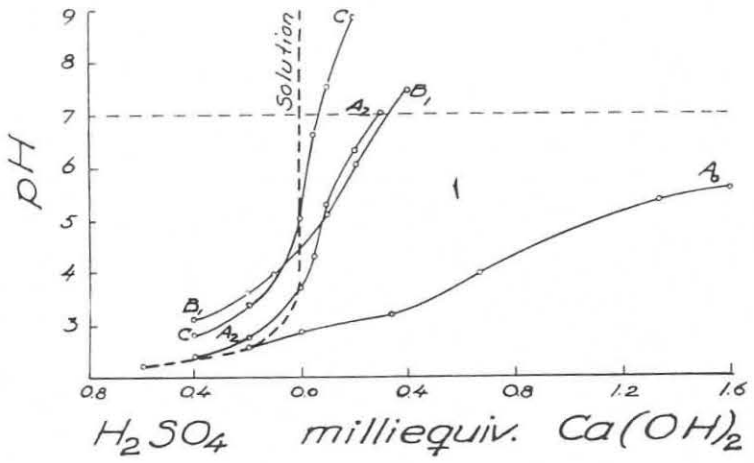


Fig. 6 b. Profile 6. (For legend, see fig. 1 b.)

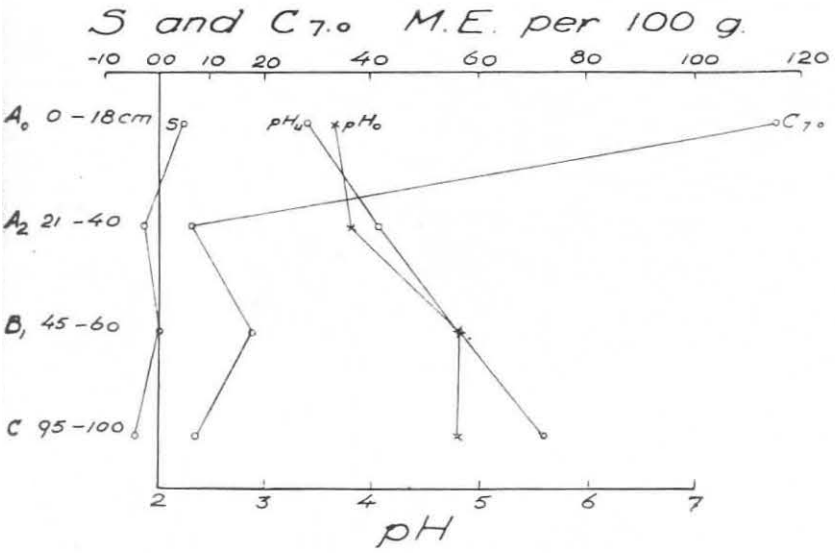


Fig. 7 a. Profile 7. (For legend, see fig. 1 a.)

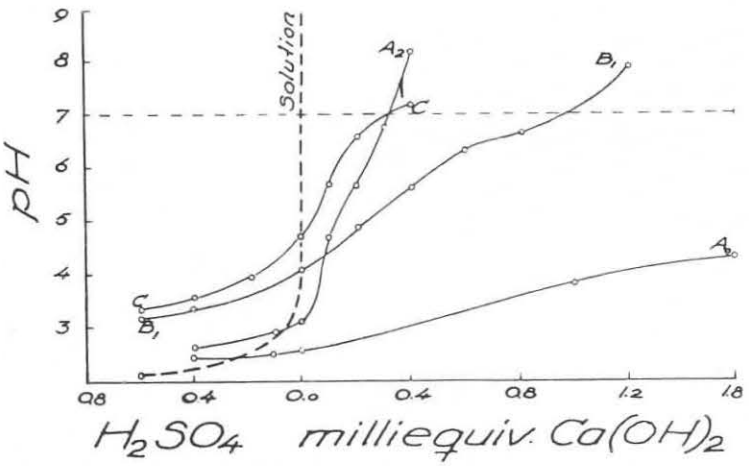


Fig. 7 b. Profile 7. (For legend, see fig. 1 b.)

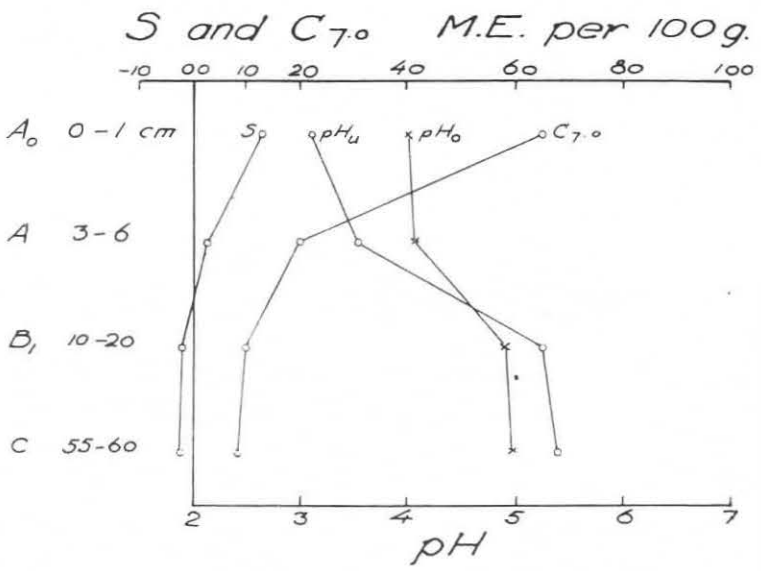


Fig. 8 a. Profile 8. (For legend, see fig. 1 a.)

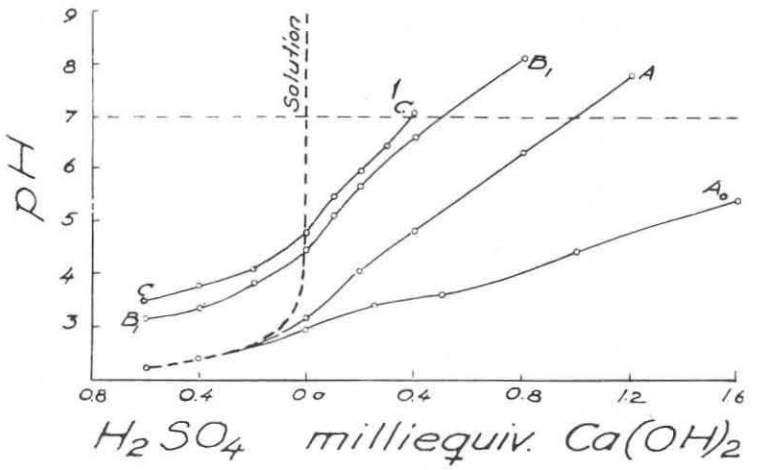


Fig. 8 b. Profile 8. (For legend, see fig. 1 b.)

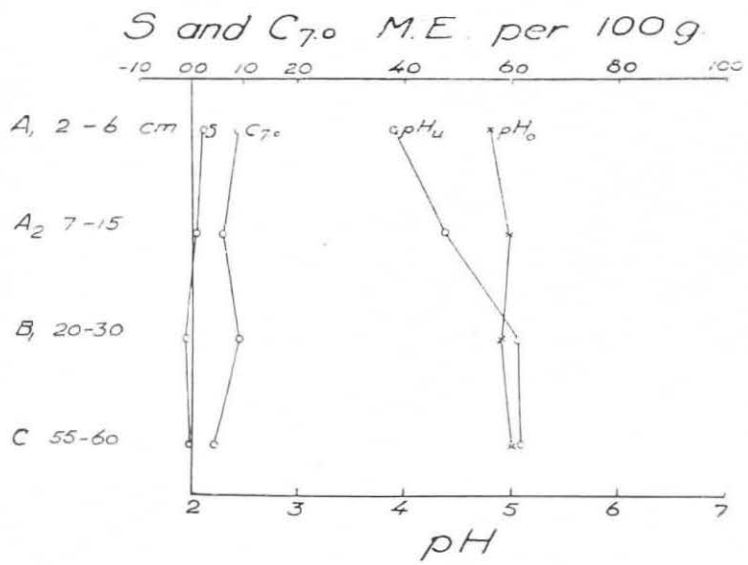


Fig. 9 a. Profile 9. (For legend, see fig. 1 a.

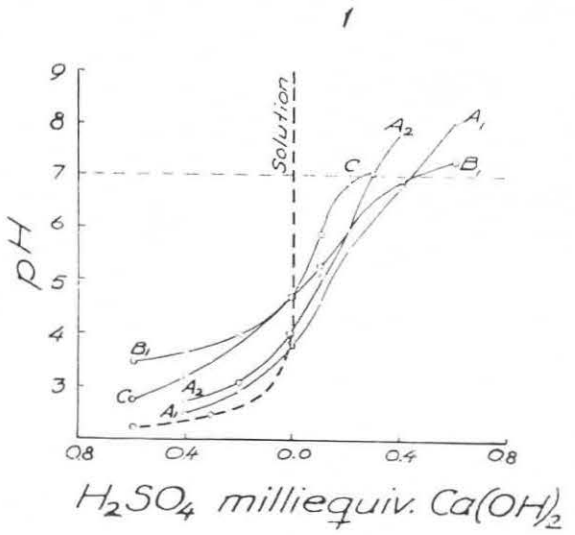


Fig. 9 b. Profile 9. (For legend, see fig. 1 b.)

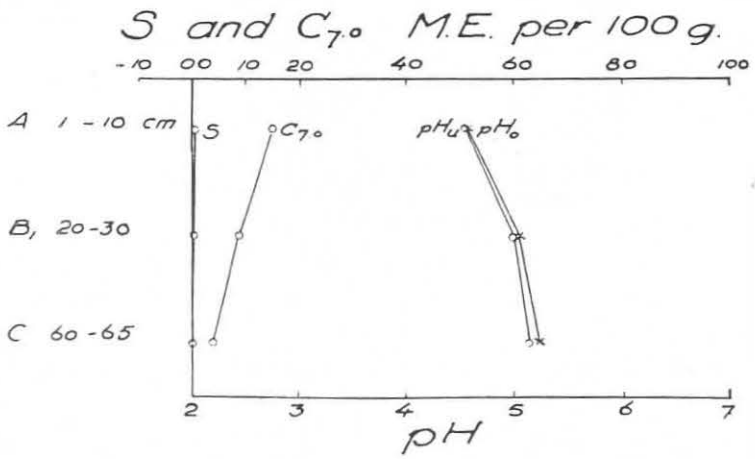


Fig. 10 a. Profile 10. (For legend, see fig. 1 a.)

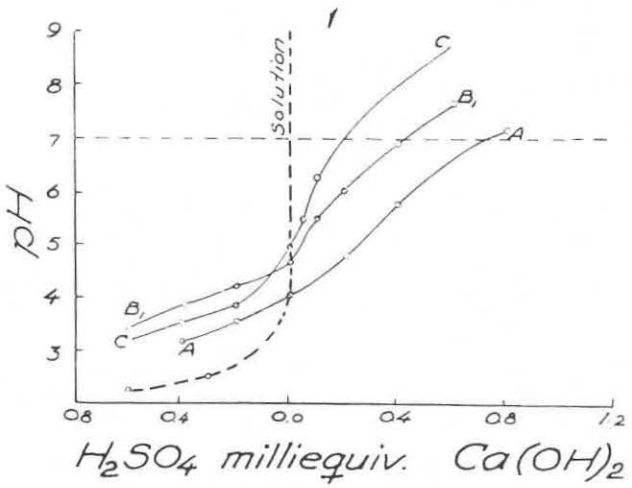


Fig. 10 b. Profile 10. (For legend, see fig. 1 b.)

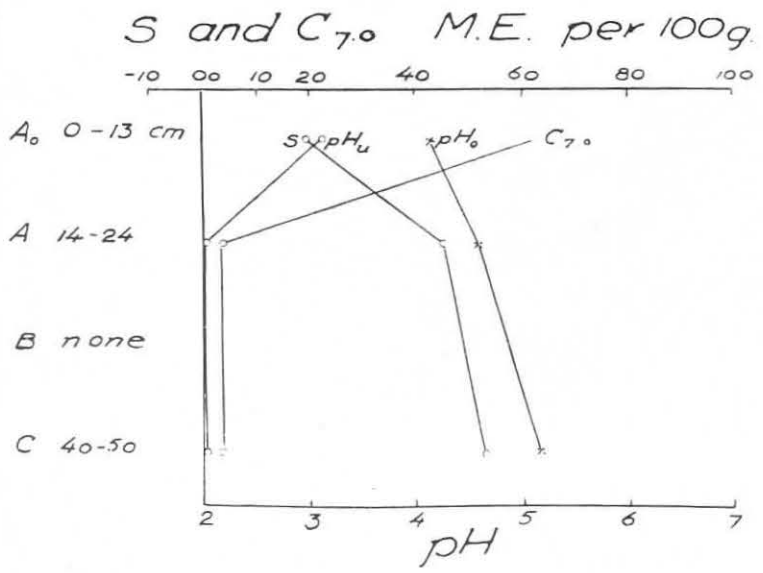


Fig. 11 a. Profile 11. (For legend, see fig. 1 a.)

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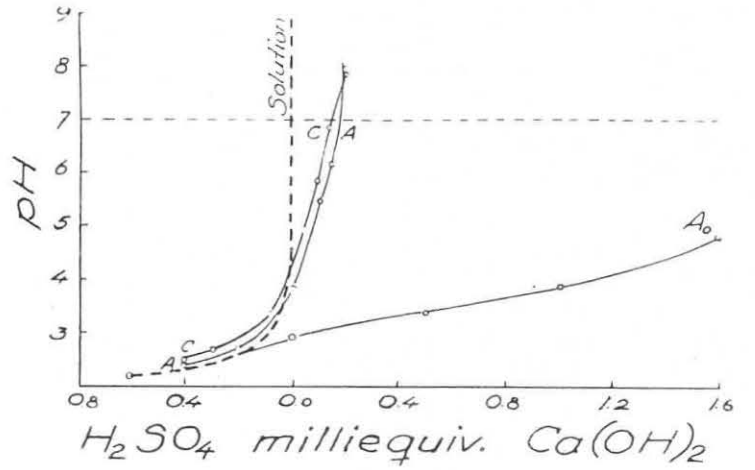

Fig. 11 b. Profile 11. (For legend, see fig. 1 b.)

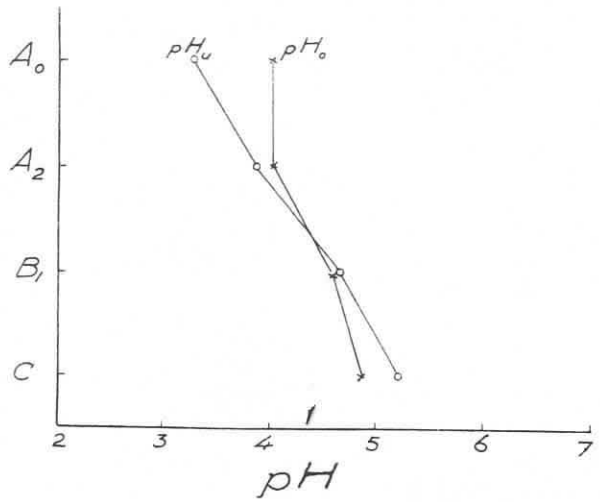

Fig. 12. The actual pH (pH_0) and the ultimate pH of the electrodialysed soil (pH_u). Average from eight true podzol profiles.

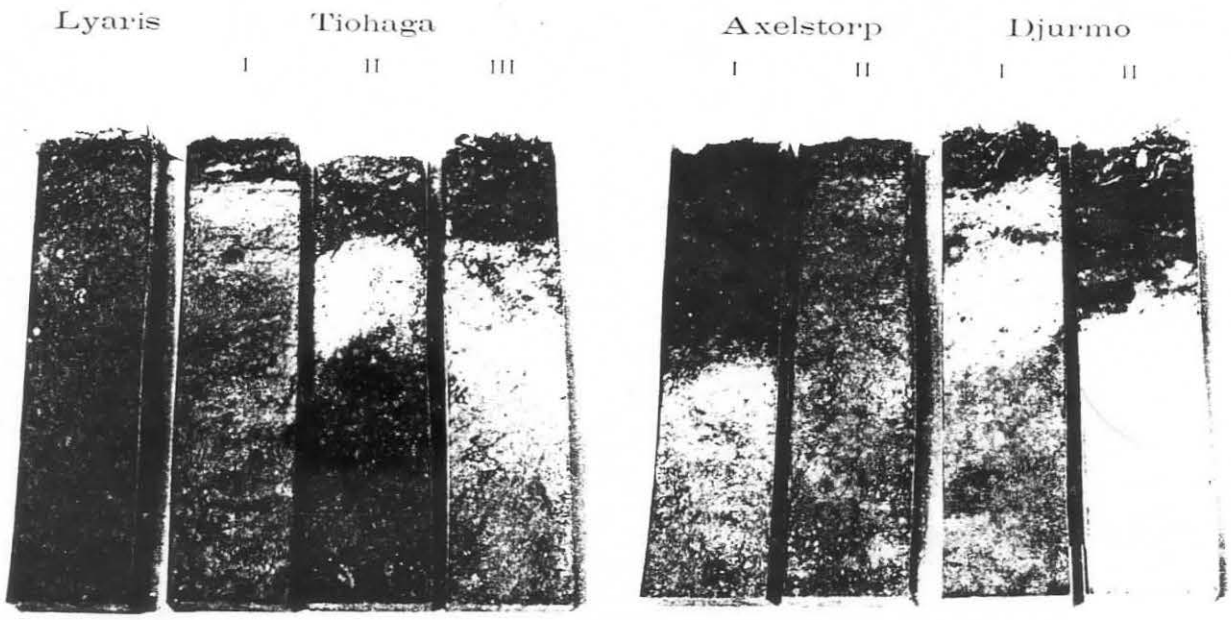

Fig. 13. Monoliths 10 × 10 cm. of profiles 10, 1, 2, 3, 7, 8, 6 and 11 from left to right.